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TITLE: EVALUATION OF RESERVOIR WETTABILITY AND ITS EFFECT ON OIL RECOVERY

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Objectives

This project has three main goals. The first is to achieve improved understanding of the surface and interfacial properties of crude oils and their interactions with mineral surfaces. The second goal is to apply the results of surface studies to improved predictions of oil production in laboratory experiments. Finally, we aim to use the results of this research to recommend ways to improve oil recovery by waterflooding.

In order to achieve these goals, the mechanisms of wetting alteration must be explained. We propose a methodology for studying those mechanisms on mineral surfaces, then applying the results to prediction and observation of wetting alteration in porous media. Improved understanding of the underlying mechanisms will show when and how wettability in the reservoir can be altered and under what circumstances that alteration would be beneficial in terms of increased production of oil.

Summary of Technical Progress

1. Crude Oil/Brine/Solid Interactions

Characterization of crude oils with respect to their ability to alter wetting based on a three-parameter profile has been proposed.[1] The profile consists of Gravity - Acid number and Base number (G-AB). API gravity represents the influence of solvent quality of the oil (which is related to gravity or density of the oil). Acidity and basicity contribute to ionic interactions between oil components and charged sites on the mineral surface. Previous investigations have shown wetting changes are greatest for very light (high gravity) oils which are poor solvents for their asphaltenes and for oils which are particularly high in acid or base number, but not both. Examples of these three types of oils which have the greatest potential to alter wettability of silica surfaces are shown in **Fig. 1**. API gravity is plotted on the vertical axis. Acid and base numbers are indicated by the horizontal bars with acid number in the negative direction and base number in the positive direction. Note that the acid numbers, which have the same units as base number, but are usually of smaller magnitude, have been multiplied by a weighting factor of four.

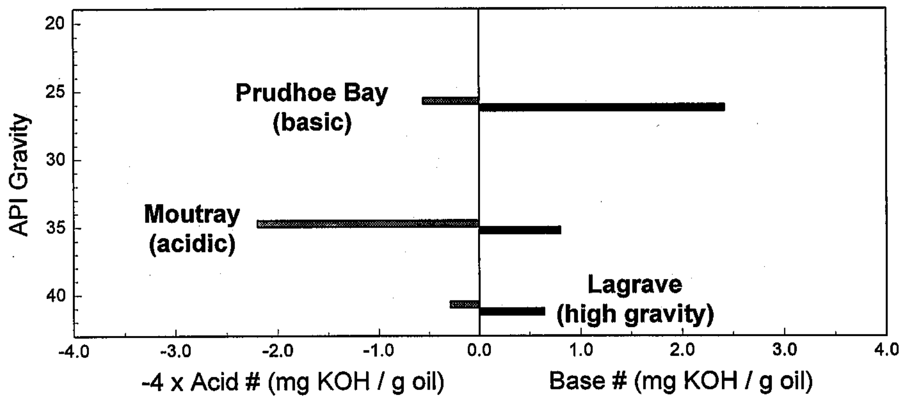

Figure 1. G-AB profiles of selected crude oils. Prudhoe Bay crude exemplifies a basic oil, Moutray is acidic, and Lagrave is a high gravity oil with asphaltenes that are approaching the onset of instability.

Most oils do not fall into one of these simple categories. If both acid and base number are low, ionic interactions may not be significant. Similarly, if both acid and base number are high, ionic interactions may be less important than if only one or the other dominates. As yet, it is not possible to put limits on the G-AB profile values to predict the extent of various types of interactions. More information is needed between the extremes represented by the oils in **Fig. 1**. In this report, evaluations of the ionic COBR interactions of four medium gravity oils, range in gravity from 27° to 31° API, are reported. Rock surfaces are represented by muscovite mica.

2. Wetting Evaluation

Crude oil samples: Properties of the four oils selected for testing are summarized in **Table 1** and **2**. Their G-AB profiles are shown in **Fig. 2**.

Table 1 Physical and Chemical Properties of Crude Oils.

	CS	Gullfaks-96	Mars-97	Spraberry
Density @ 25°C (g / mL)	0.8861	0.8856	0.8811	0.8635
RI @ 20°C	1.5029	1.4930	1.4950	1.47824
P_{RI} with n-C_7	n/a	n/a	1.4316	n/a
Asphaltene ppt with n-C_5 (wt%)	1.38	1.13	3.25	0.39
Asphaltene ppt with n-C_7 (wt%)	0.48	0.56	1.86	0.16

Table 2. Crude Oil G-AB Parameters.

	CS	Gullfaks-96	Mars-97	Spraberry
API gravity @ 60°F	27.0°	28.3°	30.3°	31.1°
Acid Number (mg KOH / g oil)	0.330	0.244	0.368	0.085
Base Number (mg KOH / g oil)	1.16	1.19	1.79	2.65
Base Number/Acid Number	3.5	4.9	4.9	31.2

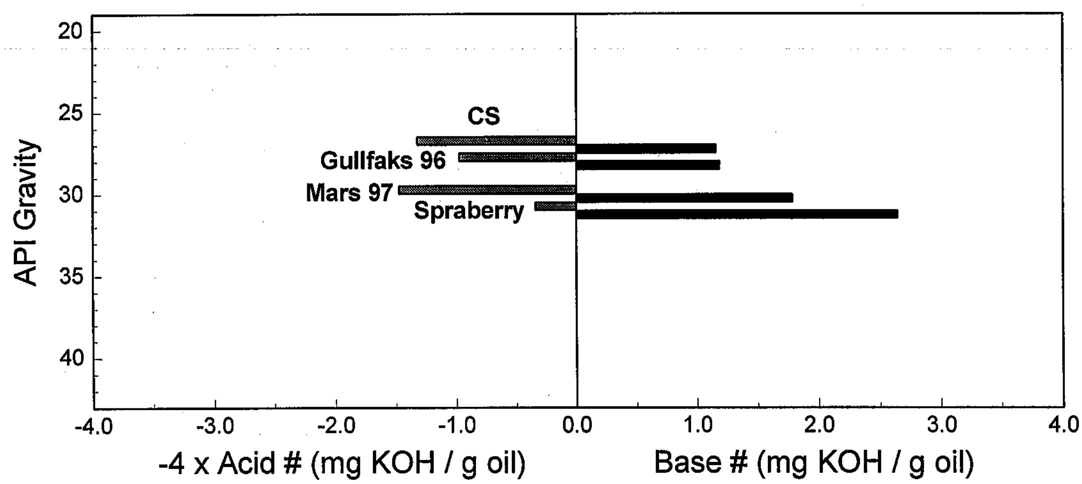

Figure 2. G-AB profiles of the four oils selected for study.

None of these oils is in the poor solvent category, exemplified by the high gravity Lagrave. We expect, therefore, that if they alter wetting, they must do so by ionic interactions, not by surface precipitation of asphaltenes.

Only one of this set of four medium gravity crude oils would be expected to have a significant impact on wetting by ionic interactions. Spraberry has a high base number (2.65 mg KOH/g oil) and a low acid number (0.085 mg KOH/g oil). The remaining three oils have acid and base numbers that fall in the median ranges, with neither base numbers nor acid numbers dominating. We thus expect that CS, Gullfaks-96, and Mars-97 will have minimal effects on the wetting of a silicate surface by any of the mechanisms identified to date. Note that Spraberry is expected to have more influence on wetting even than Mars-97, which has 3.25% *n*-pentane asphaltenes.

Brine compositions: Each oil was tested with several brines. Reservoir brines were prepared for CS and Spraberry. Synthetic sea water was used to test Gullfaks-96 and Mars-97. In each case, additional compositions were prepared by diluting these base brines to one-tenth and one-hundredth strength. For Spraberry, additional compositions with decreased NaCl concentration (referred to as reduced NaCl reservoir brine or RRB) were also tested. Details of the base brine compositions are listed in Table 3.

Table 3. Brine Compositions.

	CS RB (*M*)	Spraberry RB (*M*)	Spraberry RRB (*M*)	Synthetic Sea Water SW (*M*)
$NaHCO_3$	0.01818			0.00046
Na_2SO_4	0.00019			0.02757
NaCl	0.22638	2.09951	0.02413	0.41073
KCl	0.00144			
$CaCl_2 \cdot 2H_2O$	0.00146	0.05110	0.05868	0.00998
$MgCl_2 \cdot 6H_2O$	0.00099			0.05236
$[Ca^{2+}] / [Na^+]$	0.006	0.024	2.432	0.021
Ionic Strength	0.25391	2.25279	0.20017	0.68093

Surface preparation: Freshly cleaved mica surfaces were equilibrated with a selected brine for up to 24 hours, after which they were aged in crude oil at either 25°C or an elevated temperature of 55° or 60°C. After aging, they were rinsed with toluene and immersed in decane.

Contact angle measurements: Treated surfaces were characterized by measurements of contact angles for a drop of water advancing over a decane-covered surface. **Figure 3** shows the contact angles measured on mica surfaces aged in CS, Gullfaks-96, or Mars-97 crude oil. The results range from a low of 20° (preferentially water-wet) to a high of 71° (nearly neutral). Surfaces aged at higher temperature are usually, but not always, less water-wet. No oil-wet surfaces were produced by any of the combinations of brine, oil, aging time, or aging temperature tested.

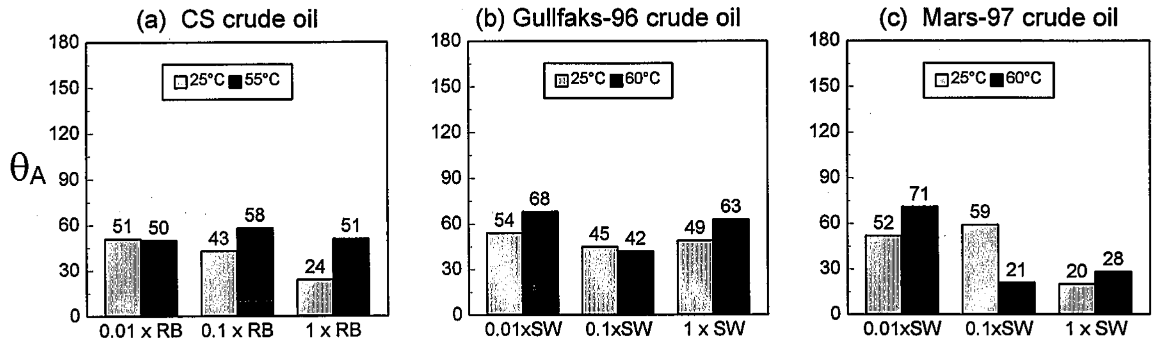

Figure 3. Water advancing angles on mica surfaces. Surfaces were treated with synthetic reservoir or sea water brines, or their ten-fold and hundred-fold dilutions, and aged for 21 days in (a) CS crude oil, (b) Gullfaks-96 crude oil, or (c) Mars-97 crude oil. Angles were measured with water and decane after removal of bulk oil by rinsing with toluene.

Similar tests are shown in **Fig. 4** for surfaces treated with Spraberry crude oil. More oil-wet surfaces were produced, especially for mica treated first with low ionic strength brine, then aged in oil at elevated temperature. Advancing angles on mica surfaces treated at 60°C are shown in **Fig. 5** as a function of the ionic strength of the pretreating brine. Additional details and test results are available.[2]

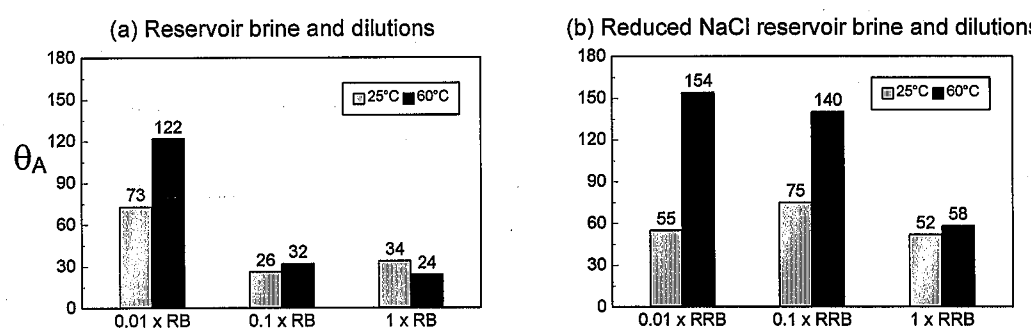

Figure 4. Water advancing angles on mica surfaces. Surfaces were treated with (a) synthetic reservoir or (b) reduced NaCl reservoir brines, or their ten-fold and hundred-fold dilutions, and aged for 21 days in Spraberry crude oil. Angles were measured with water and decane after removal of bulk oil by rinsing with toluene.

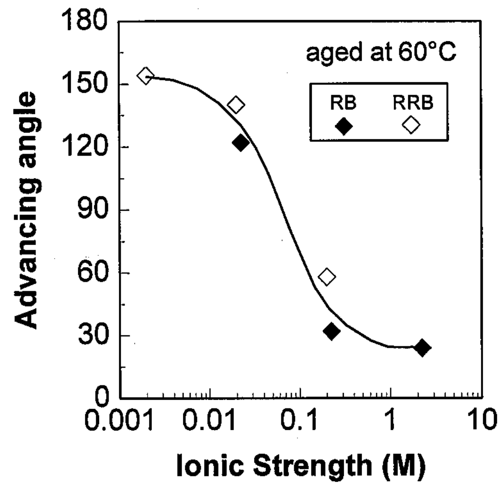

Figure 5. On Spraberry-treated mica surfaces, water advancing angles vary with ionic strength of the pre-treatment brine.

Conclusions: The results of wettability tests with these four medium gravity oil samples are consistent with expectations based on their G-AB profiles. Surface precipitation should not be an important factor for any of these samples. Spraberry, with a high base number and low acid number, participates in acid/base interactions with the acidic mica surface. These interactions are strongest when ionic strength is low.

As additional experience is gained with oils that have an increasingly wide range of G-AB profiles, we expect to be able to define more closely the properties associated with oils that have the highest and lowest propensity to alter wetting of solid surfaces.

References

1. Buckley, J.S., Liu, Y., and Monsterleet, S.: "Mechanisms of Wetting Alteration by Crude Oils," paper SPE 37230 presented at the 1997 SPE International Symposium on Oilfield Chemistry, Houston, 18-21 Feb.
2. Chang, V. and Buckley, J.S.: "COBR Interactions of Some Medium Gravity Crude Oils," PRRC # 98-4.